Study of Co-phthalocyanine films by surface plasmon resonance spectroscopy

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We present a Surface Plasmon Resonance spectroscopy study of Co-Phthalocyanine (CoPc) thin films grown on Au layers at different substrate temperatures. We demonstrate that for quantitative analysis, fitting of the resonance angle alone is insufficient and Whole Curve Analysis (WCA) needs to be performed. This is because CoPc thin film dielectric constant and thickness are strongly affected by substrate temperature, even when the total deposited mass remains fixed. Using WCA, we are able to uniquely fit both the dielectric constants and the thicknesses of the films without making *a priori* assumptions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868160]

INTRODUCTION

Surface Plasmon Resonance (SPR) is an outstanding property of metallic nanostructures, consisting of a collective oscillation of conduction electrons at the metal/dielectric interface.[1,2] For thin films, the SP corresponds to transversal oscillations that propagate along the interface and decay exponentially perpendicular to the interface.[1,3–6] These collective oscillation modes are highly sensitive to the properties of the dielectric medium close to metallic thin film leading to applications in fields as sensing,[7] biomedicine,[8] energy,[9] and optoelectronics.[4]

SPR spectroscopy is commonly performed using the Kretschmann-Raether configuration[1] depicted in the inset of Fig. 1(a). In this configuration, a metallic thin film (typically 50 nm of Au or Ag) is illuminated from the backside through a glass prism at total internal reflection conditions. The reflectivity from the metal film is then measured as a function of the incidence angle. This shows a minimum at an angle for which the SP dispersion relation is matched.

Most SPR studies analyze the resonance angle to determine either the thickness (d) or the dielectric constant ($\varepsilon = \varepsilon_1 + i\,\varepsilon_2$) of the film, if the other value is known. This is useful for inorganic systems where the dielectric properties and the density are scarcely dependent on growth conditions (i.e., substrate temperature, deposition rate, etc.). However, in some systems neither ε nor d can be determined *a priori*. In such cases, different combination of ε and d can produce the same resonance angle and reflectivity as illustrated in Fig. 1.

Organic Co-Phthalocyanine (CoPc) thin films are an interesting case where the determination of d and ε is not straightforward. These organic films show high sensitivity to the growth conditions[10–12] as well as to the interactions with the substrate[13] and the surrounding media.[14,15] Their optical properties have been studied extensively by different techniques.[16–21] However, as shown in Table I, there is a large disagreement in the reported values of ε when measured at 632.8 nm. The determination of the thickness of very thin CoPc films ($d < 50$ nm) is also difficult because the low reflectivity of these materials makes difficult to obtain well defined X-ray interference patterns. We show here that for such cases SPR spectra need to be fitted using Whole Curve Analysis (WCA), which allows determining simultaneously and uniquely both the thickness and dielectric constant.

EXPERIMENTAL

Au/CoPc bi-layers samples were prepared in an Organic Molecular Beam Epitaxy system with a base pressure of 1×10^{-10} Torr. Au films of 50 nm were deposited on soda-lime glass substrates (1 mm thick) using electron beam physical vapor deposition. A CoPc thin film was thermally deposited covering only half of the sample (Fig. 2). A total of four samples with CoPc films with nominal thicknesses between 2 and 5 nm were prepared on substrates kept at room temperature (RT) and at 200 °C. The Au and CoPc thicknesses were controlled with a quartz crystal microbalance, which was calibrated using X-ray reflectometry.

The SPR spectra were measured using the Kretschmann-Raether configuration[1,6] (inset of Fig. 1(a)) with a home-made device described elsewhere.[22] The SPR was excited using a 632.8 nm laser; the angular response of the photodiode was corrected as described in Ref. 23. For each sample a minimum of 6 scans were recorded at different position on the sample. The spectra we present correspond to the average of these scans where the line thickness indicates the standard deviation. Any possible drift in the motor positions was corrected by fixing the position of the critical angle to 42.6°; this value depends only on the quartz prism and the surrounding air and it is independent of the Au and CoPc films. SPR curve simulations were carried out using Winspall freeware by RES-TEC[24] including the correction of the refraction for triangular prisms. Fits were performed using 500 iterations with

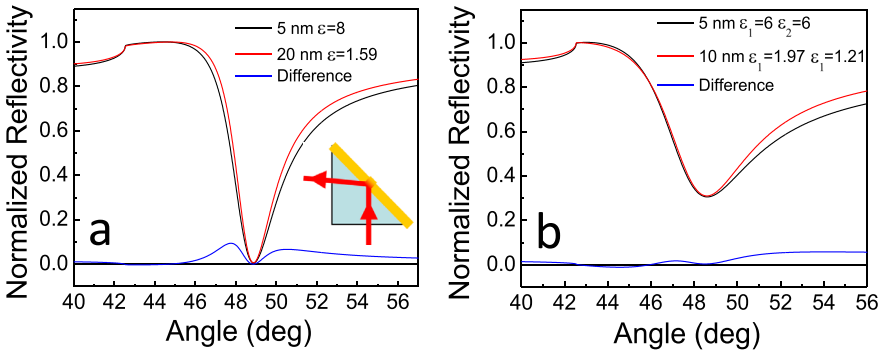

FIG. 1. (a) Calculated SPR spectra for dielectric films (deposited onto 50 nm Au) with different dielectric permittivity and thickness showing identical resonance angle and intensity and their difference for: (a) real and (b) complex dielectric permittivity. Inset shows the Kretschmann-Raether scattering geometry.

the CoPc film thickness and the dielectric constant being free parameters.

RESULTS AND DISCUSSION

Accuracy of the WCA

To estimate the accuracy of the WCA, we fit the SPR spectrum of a CoPc film with a nominal thickness of 5 nm using d and ε as free parameters (see Fig. 3). The best fit corresponds to $d = 5.16$ nm and a dielectric permittivity of $\varepsilon_1 = 3.33$, $\varepsilon_2 = 3.26$. If we fix the thickness to be $\pm 10\%$ of the obtained value (i.e., 5.68 nm or 4.62 nm) and fit only the dielectric constant, a similar agreement between the experimental and the calculated spectrum (shown in Fig. 3) is not possible. The fit using thickness and dielectric constant as free parameters provides a divergence value of 0.71 while those fits obtained fixing the value of the thickness to be 5.68 nm and 4.62 nm had a divergence of 0.82 and 0.83, respectively. Similarly, if dielectric constant is varied $\pm 10\%$ of the best fit, one cannot obtain a good fit for any thickness (not shown). This indicates that (1) the SPR technique provides an estimate of the film thickness and dielectric constant more accurately than other techniques and (2) WCA allows the simultaneous determination of the film thickness and dielectric constant.

Au films

The quality of the Au film, in particular its thickness and roughness, may cause variations in the SPR spectrum profile.[25–27] To correct for this we measured the SPR spectra in the bare Au regions of the samples. Fig. 4(a) shows that the SPR spectra are nearly identical for all of the samples and can be fitted using the dielectric constant of the glass substrate $\varepsilon_s = 2.12$, the Au thickness, $d = 49.45$ nm, and dielectric permittivity $\varepsilon_1 = -11.98$ and $\varepsilon_2 = 1.26$ (see Fig. 4(b)). The fitted dielectric permittivity is in very good agreement to the value reported for Au.[28] These results allow us to carry out numerical analysis of the SPR curves by assuming that the Au films parameters are identical for all the samples.

Thickness effects

Very thin metal-phthalocyanine (MPc) films on metallic substrates exhibit many unusual properties. For example, the electrical conductivity of CoPc and CuPc capacitive devices depends exponentially on the film thickness.[29] Charge transfer between the substrate and the organic film has been reported for CoPc grown on Au films.[30–33] The charge transfer is limited to the first CoPc layers and consequently the overall effect is thickness dependent. *In situ* transistor field effect transport during CuPc film growth shows a decrease in the electron mobility as the layer thickness increases.[34] Finally, CuPc films on metallic substrates show variations in the occupation of electronic levels at the Fermi level when the organic layer thickness is below ~10 nm.[35,36]

We explored the thickness dependence of the dielectric constant in CoPc. Fig. 5 shows the SPR spectra for nominally 2 and 5 nm thick CoPc films grown at RT. The SPR spectrum for the 2 nm film has a resonance angle at 47.2°. This curve can be fitted with a 1.93 nm CoPc film thickness and a dielectric constant of $\varepsilon_1 = 6.46$ and $\varepsilon_2 = 6.38$. In the 5 nm CoPc film, the resonance is at 48.1°. In this case, the best fit is obtained with 5.16 nm CoPc thickness and a dielectric constant of $\varepsilon_1 = 3.33$ and $\varepsilon_2 = 3.26$ values. For both samples, the difference between the nominal and the fitted thickness is below 5%. This difference is within the experimental error of the quartz microbalance used to determine thickness during growth. The dielectric constant of the 5 nm film is significantly smaller than that obtained for the 2 nm film. We also verified that it is not possible to obtain a

TABLE I. Reported values of the dielectric function for cobalt phthalocyanine at 632.8 nm.

Thickness (nm)	Substrate	Deposition	Technique	ε_1	ε_2	Reference
100-1000	Silicon crystal	Vacuum sublimation	Ellipsometry	1.92	2.56	16
100-500	Quartz	Thermal evaporation	Reflectance and transmittance	1.23	3.74	17
48	Quartz, glass & silicon	Thermal evaporation	Ellipsometry and absorbance	3	2.6	18
257	Au films	Thermal evaporation	Absorbance and reflectance	2.8	4.7	19
2-11	Au and Ag films	Thermal evaporation	Surface plasmon-ATR	5.8	4.8	20
11	Au film	Thermal evaporation	Surface plasmon-ATR	6.7	4.5	21

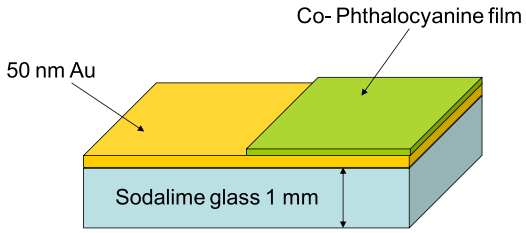

FIG. 2. Sample geometry.

reasonable fit of the SPR curve for the 5 nm thickness film using the value of dielectric permittivity obtained for the 2 nm CoPc (in this case the divergence of the fit results in a non-acceptable value of 1.91).

These results show that for CoPc films below ~5 nm the dielectric permittivity of the CoPc film is thickness dependent. This strong dependence of the permittivity on CoPc thickness is in agreement with the previous works.[29–34] Previous studies demonstrated that the orientation of the CoPc molecules may vary with the thickness, changing from parallel to perpendicular to the substrate.[37] This effect strongly depends on the type of substrate and it will certainly affect to the dielectric properties and SPR curves of the CoPc films. In our case, CoPc molecules grown parallel to the substrate as demonstrated by NEXAFS measurements.[38] Thus, in our experiments the thickness dependence of the dielectric permittivity of the CoPc is mostly related to the interaction with the substrate. However, for other preparation methods, the anisotropic growth must be considered when analysing the thickness dependence of the dielectric properties of the CoPc films.

Deposition conditions effects

The morphology (grain size, roughness, and crystalline phase) of MPc films depends on the substrate temperature during the deposition.[10–12] Substrate temperature controls the formation of grains with distinct molecular arrangements;[10,39,40] films deposited on substrates at RT are oriented in the α-phase, while films deposited at above 150 °C yield

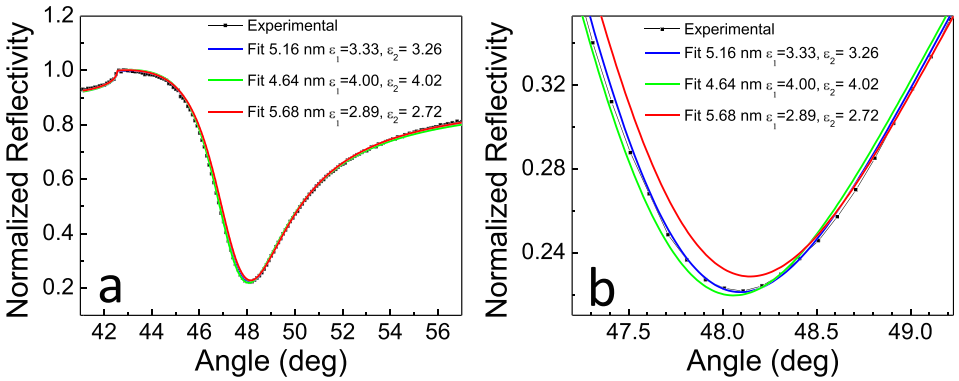

FIG. 3. (a) SPR spectrum for a CoPc film (5 nm nominal thickness) deposited onto 50 nm Au and the fit obtained with thickness and ε as free parameters (blue line) and the fits obtained fixing the thickness to be 5.68 nm (red line) and 4.64 nm (green line). (b) Details of the resonance region.

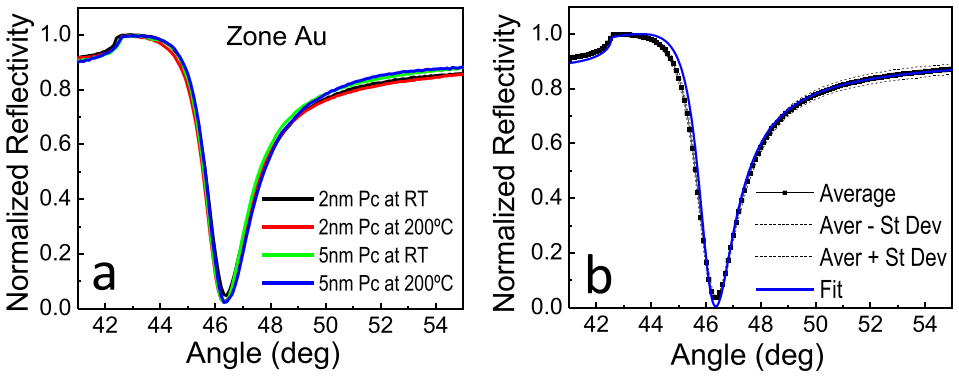

FIG. 4. (a) Comparison of SPR spectra of the bare Au region of the four CoPc samples. (b) Average SPR spectrum (± standard deviation) of the samples and fits corresponding to a 50 nm Au film over sodalime glass substrate.

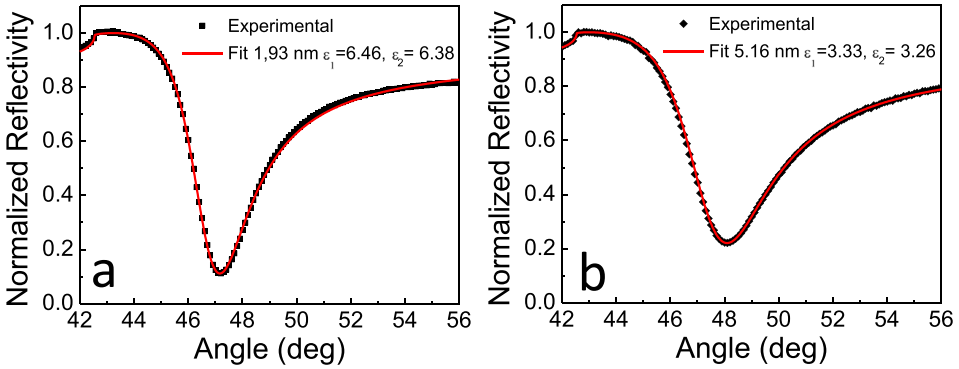

FIG. 5. Experimental SPR spectra of (a) 2 nm and (b) 5 nm thickness of CoPc films growth at RT and their corresponding fits. Fitting parameters are indicated in the graphs.

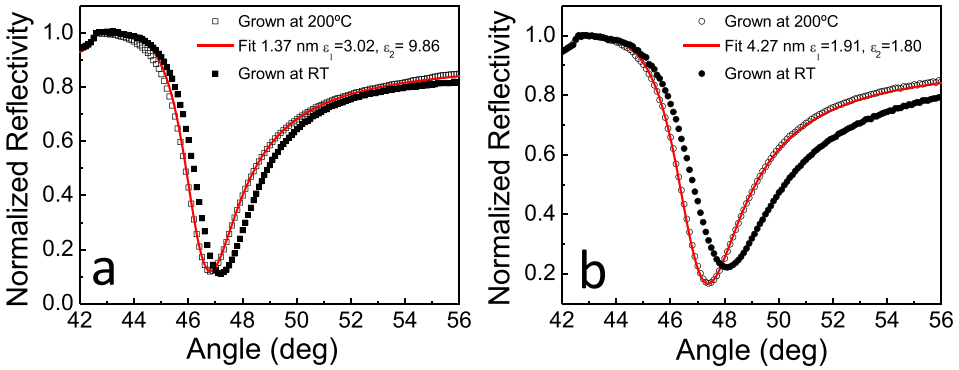

FIG. 6. Experimental SPR spectra of (a) 2 nm and (b) 5 nm nominal thicknesses of CoPc films grown at 200 °C (empty symbols) and their corresponding fits (red line) with the parameters indicated in the graph. Experimental SPR spectra for the equivalent samples grown at RT (filled symbols) are shown for comparison.

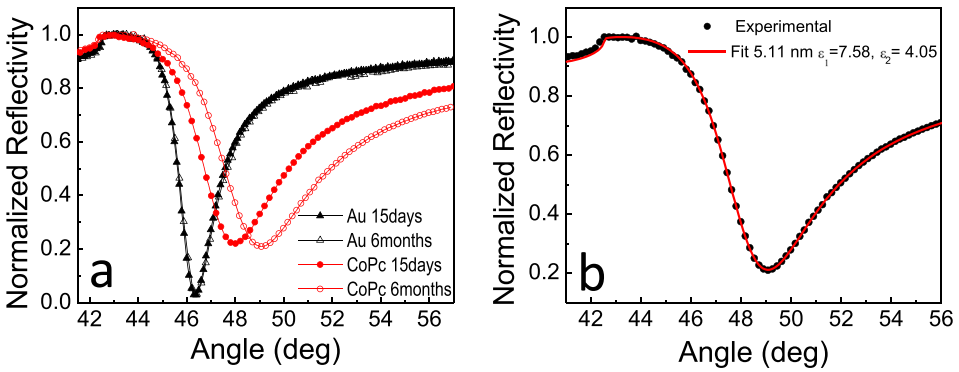

FIG. 7. (a) SPR spectra of the 5 nm CoPc sample prepared at RT obtained 15 days and 6 months after deposition and measured in the region of bare Au film and that with the CoPc film. (b) The experimental SPR spectra of the CoPc region after 6 months and the fit with the parameters indicated in the graph.

to the appearance of grains oriented in the β-phase.[10,41] These phases exhibit different optical properties, so we explored the effect of deposition temperature on the dielectric constant.

Fig. 6 shows SPR spectra for CoPc films deposited at different temperatures. The samples grown at 200 °C show a shift in the resonance toward smaller angles compared to samples grown at RT. The fittings of the 2 nm sample grown at 200 °C are $d = 1.37$ nm and $\varepsilon_1 = 3.02$, $\varepsilon_2 = 9.86$ (see Fig. 6(a)). The fitting of the 5 nm sample grown at 200 °C are $d = 4.27$ nm and $\varepsilon_1 = 1.91$, $\varepsilon_2 = 1.80$ (see Fig. 6(b)). A comparison of these results with the fits obtained for the same nominal thickness samples at RT (Figs. 5(a) and 5(b)) shows that both the thickness and the dielectric constant depend on the substrate temperature. In particular, the thickness of samples grown at 200 °C tends to be smaller than the ones at RT, indicating that films grown at higher temperature are denser in agreement with previous results.[10] For the 2 nm thick samples, the real part of the dielectric constant is reduced by 50% when the film is grown at 200 °C, while the imaginary part is increased by 50% compared to same thickness RT samples. For 5 nm thick samples grown at 200 °C, both the real and imaginary parts of the dielectric permittivity are reduced by about 45% compared to the same thickness samples grown at RT. These results confirm that deposition temperature related changes in the morphology of the CoPc films have significant impact on the dielectric constant of the films.

Aging effects

MPcs are very sensitive to small traces of chemical vapors and gases. This property led to applications in electronic and optical chemical sensors.[7] Due to this chemical sensitivity, MPc transport properties degrade on the timescale of day when exposed to ambient conditions.[42]

Fig. 7(a) shows the SPR spectra of the 5 nm sample prepared at RT recorded 15 days and 6 months after the deposition. Between these two measurements the samples were stored in darkness and exposed to air. While the spectrum corresponding to the bare Au region does not change, significant differences appear for the CoPc film. After 6 months, the resonance shifted from 48.1 to 49.1° and the reflectivity at the resonance angle increased slightly. The SPR spectrum for the 6 month old sample can be fitted with 5.11 nm thickness and a dielectric function $\varepsilon_1 = 7.58$, $\varepsilon_2 = 4.05$ (see Figs. 5(b) and 7(b)), while the spectrum obtained for the same sample 15 days after preparation corresponded to 5.16 nm and $\varepsilon_1 = 3.33$, $\varepsilon_2 = 3.26$. The thickness is almost identical to that initially measured (5.16 nm), confirming that there is no material removal or evaporation in the interim. However, there is a significant increase in the dielectric constant, especially in the real part. This could be related to the degradation of phthalocyanine due to the absorption of gases and chemical vapors present in the air.

CONCLUSIONS

Our study demonstrates that limiting the analysis of the SPR curves only to the resonance angle and reflectivity can cause significant errors in the thickness and dielectric constant calculations. This limitation can be avoided by analysing the whole SPR curve. To demonstrate the capabilities of this approach, we studied sub-10 nm CoPc thin films. In this organic system, the thickness and dielectric constant are difficult to determine. We found that the dielectric constant

depends on the film thickness, deposition temperature, and aging, which is in agreement with previous results. Furthermore, we have observed that for a fixed amount of deposited material, films grown at 200 °C are thinner (more dense) that those grown at room temperature. This demonstrates the importance of Whole Curve Analysis for the study of organic materials and also highlights the sensitivity of organic material electronic properties to the fabrication process, thickness, and aging.

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